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Synthesis and X-ray Crystal Structures of Heavy-Metal Complexes of 1,5,9,13-Tetrathiacyclohexadecane[1]

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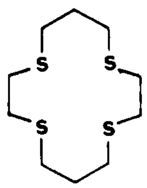
Heavy-metal complexes of the macrocyclic tetrathioether 1,5,9,13-tetrathiacyclohexadecane (16S4) have been prepared by reaction of the ligand with the appropriate heavy-metal salts. The complexes $[Hg(16S4)](ClO_4)_2$, $[Cd(16S4)](ClO_4)_2$, and $(16S4)(HgCl_2)_2$ have been synthesized and characterized. Single-crystal X-ray structural studies have been carried out on $[Hg(16S4)](ClO_4)_2$ and $[Cd(16S4)](ClO_4)_2$. Crystal data for $[Hg(16S4)](ClO_4)_2$: $C_{12}H_{24}S_4HgCl_2O_8$; monoclinic space group $C2/c$; $a = 10.033$ (3), $b = 13.421$ (4), $c = 15.960$ (4) Å; $\beta = 96.48$ (2)°; $Z = 4$; $R = 0.051$. Crystal data for $[Cd(16S4)](ClO_4)_2$: $C_{12}H_{24}S_4CdCl_2O_8$; triclinic space group $P\bar{1}$; $a = 8.346$ (2), $b = 8.349$ (3), $c = 8.688$ (2) Å; $\alpha = 69.87$ (2), $\beta = 68.97$ (2), $\gamma = 82.33$ (2)°; $Z = 1$; $R = 0.043$. Molecular mechanics calculations have been carried out on the 16S4 ligand, and the lowest energy conformation is a quadrangular [4444] conformation with the sulfur atoms occupying the corners (*exodentate*) of the quadrangle.

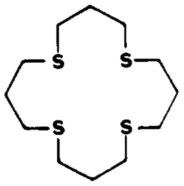
Introduction

Thioether ligands have been identified as possible selective metal extraction agents for "soft" metal ions such as lead and mercury[3] and, as such, may have important utility in terms of sequestering agents for treatment of heavy-metal poisoning.[4] In order to gain insight into the effects on coordination geometry and complex stabilities as a function of ring size, chelate ring size, and functional group substituent in mesocyclic and macrocyclic polythioether ligands, we have synthesized[5] and studied[6] a number of sulfur-containing cyclic compounds. Not only are chelate ring size and ring cavity size important in complexing abilities and complex stabilities involving heterocyclic ligands but conformational preference of the uncomplexed ligand is also important.[7] Indeed, the absence of "preorganization"[8] in macrocyclic polythioethers may be the reason for the relative lack of effectiveness of these materials as sequestering agents as compared to acyclic analogues.[4d,9] Thus, for example, 2,5,9,12-tetrathiatridecane, a linear acyclic tetrathioether, is a more effective ligand than either of the macrocycles 1,4,8,11-tetrathiacyclotetradecane (14S4) or 1,5,9,13-tetrathiacyclohexadecane (16S4) for complexing $CH_3HgOCOCF_3$.[4d]

In this paper, we report the preparation of heavy-metal complexes of the macrocyclic tetrathioether 1,5,9,13-tetrathiacyclohexadecane (16S4). The complexes $[Hg(16S4)](ClO_4)_2$, $[Cd(16S4)](ClO_4)_2$, and $(16S4)(HgCl_2)_2$ have been prepared and characterized by IR spectroscopy and elemental analysis. The crystal and molecular structures of $[Hg(16S4)](ClO_4)_2$[10] and $[Cd(16S4)](ClO_4)_2$ have been determined by single-crystal X-ray techniques. In addition, a conformational analysis of the macrocycle, 16S4, has been carried out by using the molecular mechanics technique.



14S4



16S4

Experimental Section

Dimethylformamide (DMF) and nitromethane were purchased from Aldrich Chemical Co. and were dried by using common methods.[11] Cesium carbonate and all metal salts were obtained from Alfa Inorganics and were used as received without additional purification. Analyses were performed by Atlantic Microlab, Inc., Norcross, GA, or by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained on a Perkin-Elmer 1330 infrared spectrophotometer.

Preparation of $[Hg(16S4)](ClO_4)_2$. A solution of 1,5,9,13-tetrathiacyclohexadecane (40.2 mg, 0.136 mmol) in 8 mL of anhydrous nitromethane was added to a solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (42.0 mg, 0.0937 mmol) in 2 mL of anhydrous nitromethane and 4 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether. The crystalline solid was dried overnight under high vacuum to give 42.9 mg (60.6% yield) of $[Hg(16S4)](ClO_4)_2$ as a colorless crystalline solid: IR (KBr) 2902, 1438, 1313, 1258, 1140–1070 (s, b, ClO_4^-), 922, 861, 774, 699, 620 (s, ClO_4^-) cm^{-1}. Anal. Calcd for $C_{12}H_{24}S_4HgCl_2O_8$: C, 20.71; H, 3.48; S, 18.42. Found: C, 20.93; H, 3.59; S, 18.30.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of $[Cd(16S4)](ClO_4)_2$. A solution of 1,5,9,13-tetrathiacyclohexadecane (39.6 mg, 0.134 mmol) in 8 mL of anhydrous nitromethane was added to a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (40.1 mg, 0.0956 mmol) in 2 mL of anhydrous nitromethane and 4 drops acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether. The crystalline solid was dried overnight under high vacuum to give 19.3 mg (30.9% yield) of $[Cd(16S4)](ClO_4)_2$ as a colorless crystalline solid: IR (KBr) 2920, 2830, 1440, 1331, 1286, 1256, 1140–1070 (s, b, ClO_4^-), 1010, 900, 858, 842, 768, 610 (s, ClO_4^-) cm^{-1}. Anal. Calcd for $C_{12}H_{24}S_4CdCl_2O_8$: C, 23.71; H, 3.98; S, 21.10. Found: C, 23.76; H, 3.98; S, 21.03.

X-ray Single-Crystal Structure Studies of $[Hg(16S4)](ClO_4)_2$ and $[Cd(16S4)](ClO_4)_2$.[12] In each study, a clear colorless crystal of the

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Table I. Crystallographic Data for $[Hg(16S4)](ClO_4)_2$ and $[Cd(16S4)](ClO_4)_2$

	$[Hg(16S4)](ClO_4)_2$	$[Cd(16S4)](ClO_4)_2$
mol formula	$C_{12}H_{24}S_4HgCl_2O_8$	$C_{12}H_{24}S_4CdCl_2O_8$
mol wt	696.04	607.85
space group	monoclinic, $C2/c$	triclinic, $P\bar{1}$
a, Å	10.033 (3)	8.346 (2)
b, Å	13.421 (4)	8.349 (3)
c, Å	15.960 (4)	8.688 (2)
α, deg	90	69.87 (2)
β, deg	96.48 (2)	68.97 (2)
γ, deg	90	82.33 (2)
V, Å^3	2135.33	530.51
Z	4	1
D(calcd), g cm^{-3}	2.165	1.903
μ, mm^{-1}	8.08	1.90
R	0.051	0.043
R_w	0.045	0.053

complex, suitable for X-ray diffraction, was mounted on a Syntex $P2_1$ auto diffractometer equipped with a scintillation counter and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The automatic centering, indexing, and least-squares routines were carried out on 15 reflections to obtain the cell dimensions that are given in Table I. The ω-scan technique over the range $4° \leq 2\theta \leq 50°$ was used to collect the data, of which those with $F \geq 2.5\sigma(F)$ were considered observed and were used in the calculations. No correction was made for absorption.

The structures were solved by the heavy-atom method. In each structure, the position of the metal atom was located from a three-dimensional Patterson map (in $[Cd(16S4)](ClO_4)_2$ the metal atom resides on a special position), and the remaining atoms were located by subsequent structure factor calculations and difference electron densityd maps. The structure was refined by full-matrix least-squares techniques.[12] The hydrogen atoms were located from electron density difference maps and added to the model. Hydrogen atom parameters were not refined for $[Hg(16S4)](ClO_4)_2$; hydrogen atom positional parameters were not refined for $[Cd(16S4)](ClO_4)_2$, but thermal parameters were refined. All non-hydrogen atoms were refined anisotropically. Thermal parameters for the ligand atoms in $[Hg(16S4)](ClO_4)_2$ show a large degree of motion for this molecule, due, perhaps, to a slight rotational disorder about the mercury atom. This thermal motion may be responsible for the relatively high R value observed for this structure.

Reaction of 16S4 with $HgCl_2$. A solution of 1,5,9,13-tetrathiacyclohexadecane (41.9 mg, 0.141 mmol) in 8 mL of anhydrous nitromethane was added to a solution of $HgCl_2$ (28.3 mg, 0.104 mmol) in a mixture of anhydrous nitromethane (1 mL) and absolute ethanol (1 mL). A colorless precipitate was immediately formed. The precipitate was washed with 5 mL of diethyl ether and vacuum-dried to give 32.1 mg (73.5% yield) of $(16S4)(HgCl_2)_2$ as a colorless powder: IR (KBr) 2905, 1404, 1334, 1296, 1253, 1182, 1130, 853, 752, 331 cm^{-1}. Anal. Calcd for $C_{12}H_{24}S_4Hg_2Cl_4$: C, 18.75; H, 3.15; S, 16.68; Cl, 9.22. Found: C, 18.29; H, 3.16; S, 17.48; Cl, 11.22.[13]

Results

The 16S4 ligand is prepared as a side product in the preparation of 1,5,9-trithiacyclododecane (12S3).[14] Thus, reaction of bis(3-mercaptopropyl) sulfide with 1,3-dichloropropane and cesium carbonate under high-dilution conditions[5,15] gives a mixture of 12S3, 16S4, and 24S6, which was separated by medium-pressure liquid chromatography (MPLC) on silica gel eluting with 20% ethyl acetate in hexane to give the purified macrocycles in a 78:14:8 ratio (Note: the elution order was 12S3, 16S4, then 24S6). The 16-membered-ring tetrathioether 16S4 has also been isolated as a side product in the synthesis of 1,5-dithiacyclooctane (8S2).[16]

Table II. Final Atomic Parameters for $[Hg(16S4)](ClO_4)_2$

atom	x	y	z	B, Å^2
Hg	0	0.12186 (5)	$^1/_4$	3.82 (3)
S1	0.0436 (4)	−0.0116 (3)	0.1393 (3)	8.4 (2)
S2	−0.1183 (3)	0.2575 (3)	0.3322 (3)	6.5 (2)
C1	0	−0.167 (2)	$^1/_4$	13 (3)
C2	0.109 (2)	−0.107 (1)	0.216 (2)	12 (1)
C3	0.202 (1)	0.045 (1)	0.114 (1)	8 (1)
C4	0.179 (2)	0.131 (2)	0.048 (1)	11 (2)
C5	−0.076 (2)	0.199 (2)	0.437 (1)	10 (1)
C6	0.017 (2)	0.349 (1)	0.330 (1)	8 (1)
C7	0	0.408 (2)	$^1/_4$	12 (3)
Cl	0.3356 (4)	0.1116 (4)	0.3950 (3)	6.7 (2)
O1	0.469 (1)	0.121 (1)	0.397 (1)	14 (1)
O2	0.261 (1)	0.128 (2)	0.3240 (9)	16 (1)
O3	0.277 (2)	0.154 (2)	0.454 (2)	29 (3)
O4	0.319 (2)	0.014 (2)	0.411 (2)	24 (2)

Table III. Final Atomic Parameters for $[Cd(16S4)](ClO_4)_2$

atom	x	y	z	B, Å^2
Cd	0	0	0	2.23 (3)
S1	−0.2623 (2)	0.0037 (2)	−0.0994 (2)	2.50 (6)
S2	−0.1027 (2)	0.2976 (2)	0.0403 (2)	2.45 (7)
C1	−0.2788 (7)	0.2334 (7)	−0.2027 (8)	3.0 (3)
C2	−0.3798 (7)	0.3320 (7)	−0.0686 (9)	3.2 (3)
C3	−0.3323 (7)	0.2766 (7)	0.0942 (8)	3.0 (3)
C4	−0.0922 (8)	0.2663 (7)	0.2549 (8)	3.3 (3)
C5	−0.0908 (8)	−0.2428 (7)	−0.2562 (8)	3.3 (3)
C6	−0.1624 (8)	−0.0601 (7)	−0.2941 (8)	3.3 (3)
Cl	−0.2991 (2)	−0.2656 (2)	0.3806 (2)	3.93 (8)
O1	−0.1682 (5)	−0.1361 (5)	0.3035 (6)	3.9 (2)
O2	−0.3055 (7)	−0.3341 (6)	0.2561 (7)	5.0 (3)
O3	−0.4581 (9)	−0.181 (1)	0.430 (2)	14.1 (8)
O4	−0.272 (2)	−0.382 (1)	0.517 (1)	17.4 (9)

Table IV. Selected Geometrical Parameters for $[Hg(16S4)](ClO_4)_2$

	Bond Lengths (Å)		
Hg–S1	2.587 (4)	C6–C7	1.50 (2)
Hg–S2	2.606 (4)	S2–C6	1.83 (2)
S1–C2	1.84 (2)	Cl–O1	1.34 (1)
S1–C3	1.85 (2)	Cl–O2	1.30 (1)
S2–C5	1.86 (2)	Cl–O3	1.29 (2)
C1–C2	1.50 (3)	Cl–O4	1.35 (3)
C3–C4	1.55 (3)	Hg–O2	2.75 (1)
C4–C5	1.42 (3)		
	Bond Angles (deg)		
S1–Hg–S1′	92.4 (2)	S2–C5–C4	109 (1)
S1–Hg–S2	91.0 (2)	S2–C6–C7	111 (1)
S1–Hg–S2′	161.6 (1)	C2–C1–C2′	116 (2)
S2–Hg–S2′	91.4 (1)	C6–C7–C6′	117 (2)
Hg–S1–C2	95.9 (7)	C3–C4–C5	115 (1)
Hg–S1–C3	94.7 (5)	O1–Cl–O2	119 (1)
Hg–S2–C5	94.9 (6)	O1–Cl–O3	119 (1)
Hg–S2–C6	94.7 (6)	O1–Cl–O4	104 (1)
C2–S1–C3	100.5 (8)	O2–Cl–O3	107 (2)
C5–S2–C6	101.8 (9)	O2–Cl–O4	105 (2)
S1–C2–C1	113 (1)	O3–Cl–O4	102 (2)
S1–C3–C4	113 (1)		

The complexes of 16S4 are conveniently prepared by mixing a solution of the ligand in nitromethane with a solution of the appropriate heavy-metal salt in nitromethane along with a small amount of acetic anhydride (to react with water of hydration present in the salt). Reaction of 16S4 with $HgCl_2$ immediately precipitates the 1:2 complex $(16S4)(HgCl_2)_2$. Reaction of the ligand with $Hg(ClO_4)_2$ or with $Cd(ClO_4)_2$ leads to 1:1 complexation, $[Hg(16S4)](ClO_4)_2$[10] and $[Cd(16S4)](ClO_4)_2$, respectively.

In order to provide more insight into the conformational properties (steric energy demands in endodentate vs exodentate

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(12) The structures were solved by D. G. VanDerveer. The programs used for the solution and refinement of the structures were those in NRCVAX from the National Research Council, Ottawa, Canada (Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, U.K., 1985; pp 167–174).

(13) Due to the insolubility of the complex, recrystallization of the product was not possible. While the elemental analysis does indicate an impure product, the approximate stoichiometry (ligand:metal) can be calculated.

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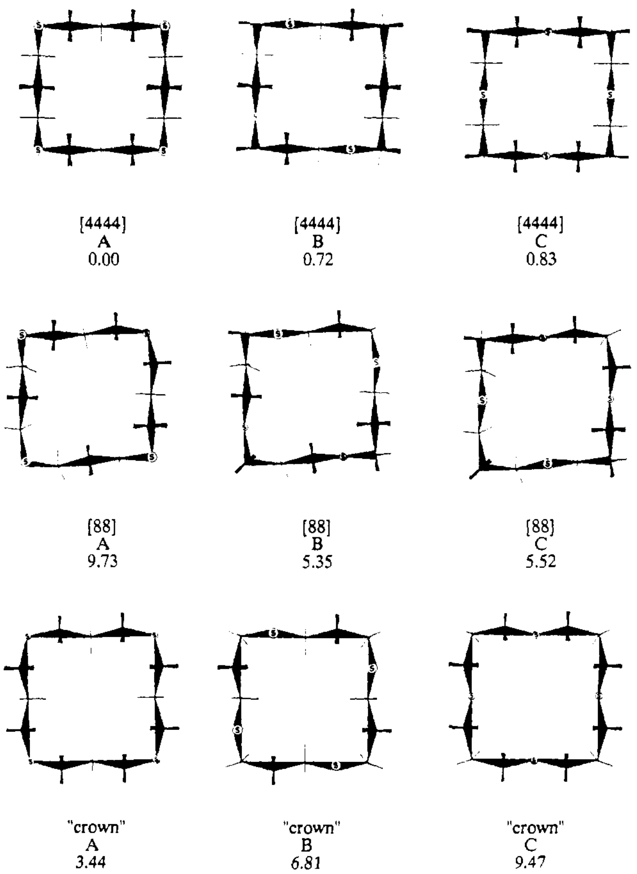
[4444]
A
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[4444]
B
0.72

[4444]
C
0.83

[88]
A
9.73

[88]
B
5.35

[88]
C
5.52

"crown"
A
3.44

"crown"
B
6.81

"crown"
C
9.47

Figure 1. Conformational analysis of 1,5,9,13-tetrathiacyclohexadecane.

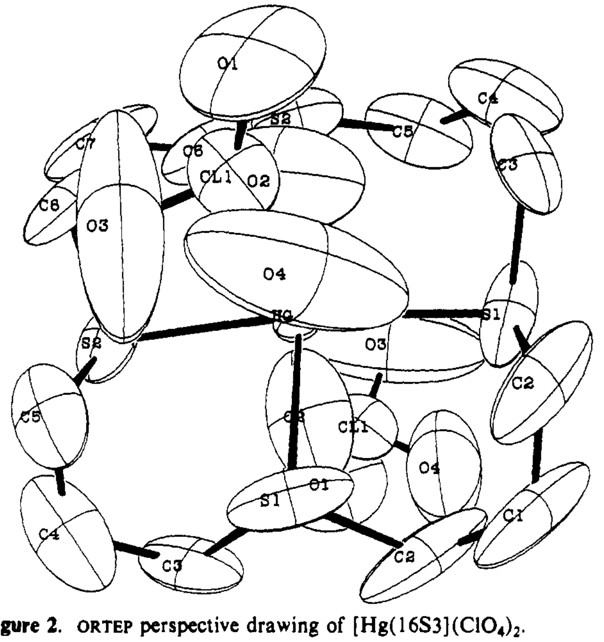

Figure 2. ORTEP perspective drawing of [Hg(16S3](ClO$_4$)$_2$.

conformations) of this macrocyclic tetrathioether ligand, we have carried out molecular mechanics calculations (using the MM2 technique[17]) on some of the conformational possibilities of this 16-membered ring. The results of these calculations are summarized in Figure 1.

Single-crystal X-ray structural studies have been undertaken for [Hg(16S4)](ClO$_4$)$_2$ and [Cd(16S4)](ClO$_4$)$_2$. ORTEP perspective drawings, from the X-ray crystal structures, of [Hg(16S4)](ClO$_4$)$_2$ and [Cd(16S4)](ClO$_4$)$_2$ are shown in Figures 2 and 3, respectively. The crystallographic data for the compounds are listed in Table I. Atomic coordinates for the non-hydrogen atoms appear in Tables II and III. Bond lengths and bond angles for the complexes are given in Tables IV and V, respectively.

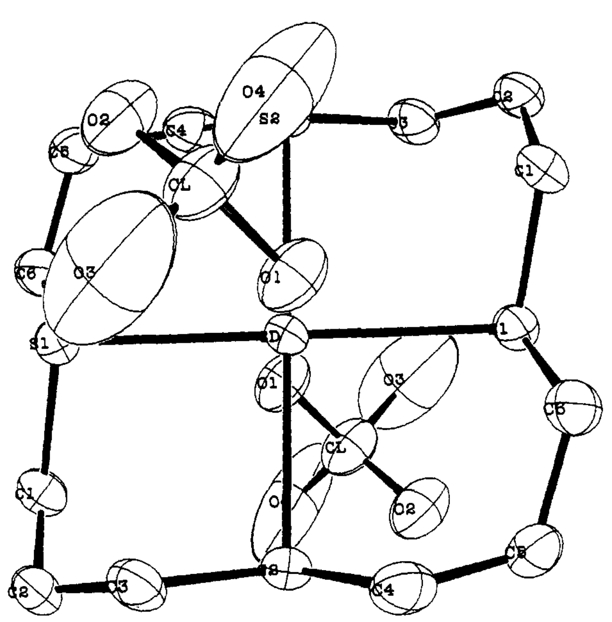

Figure 3. ORTEP perspective drawing of [Cd(16S4)](ClO$_4$)$_2$.

Table V. Selected Geometrical Parameters for [Cd(16S4)](ClO$_4$)$_2$

	Bond Lengths (Å)		
Cd–S1	2.619 (1)	C5–C6	1.531 (8)
Cd–S2	2.616 (2)	S2–C4	1.825 (6)
S1–C1	1.827 (5)	Cl–O1	1.450 (4)
S1–C6	1.825 (6)	Cl–O2	1.406 (5)
S2–C3	1.820 (6)	Cl–O3	1.414 (8)
C1–C2	1.529 (9)	Cl–O4	1.319 (7)
C2–C3	1.514 (9)	Cd–O1	2.434 (4)
C4–C5	1.517 (9)		
	Bond Angles (deg)		
S1–Cd–S1′	180.0	S2–C3–C2	111.2 (4)
S1–Cd–S2	88.51 (5)	S2–C4–C5	112.2 (4)
S1–Cd–S2′	91.49 (5)	C1–C2–C3	117.3 (4)
S2–Cd–S2′	180.0	C4–C5–C6	116.7 (5)
Cd–S1–C1	98.9 (2)	Cd–O1–Cl	130.3 (3)
Cd–S1–C6	101.9 (2)	O1–Cl–O2	110.9 (3)
Cd–S2–C3	99.1 (2)	O1–Cl–O3	106.2 (4)
Cd–S2–C4	102.0 (2)	O1–Cl–O4	109.1 (4)
C1–S1–C6	99.2 (3)	O2–Cl–O3	106.0 (5)
C3–S2–C4	100.5 (3)	O2–Cl–O4	113.4 (5)
S1–C1–C2	111.3 (4)	O3–Cl–O4	111.0 (8)
S1–C6–C5	113.3 (4)		

Discussion

On the basis of X-ray structural analyses of macrocyclic polythioethers,[5,7b–d,18] the preferred conformation for 16S4 is expected to be a quadrangular structure with the sulfur atoms occupying corners of the quadrangle: a [4444] conformation with the sulfur atoms *exodentate* (see Figure 1, conformation [4444]A). The [4444] conformation has been found to be the lowest energy conformation for cyclohexadecane by strain-energy calculations,[19] in agreement with the solid-state conformation.[20] The X-ray

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[17] (a) For a discussion of the molecular mechanics technique, see: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982. (b) We used the program CHEM CAD, suitable for the IBM PC, available from C Graph Software, Inc., Austin, TX. This software package includes Allinger's MM2.

[18] (a) Setzer, W. N.; Cacioppo, E. L.; Grant, G. J.; Glass, R. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *45*, 223. (b) Dalley, N. K.; Larson, S. B.; Smith, J. S.; Matheson, K. L.; Izatt, R. M.; Christensen, J. J. *J. Heterocycl. Chem.* **1981**, *18*, 463. (c) Ammon, H. L.; Bhattacharjee, S. K.; Shinkai, S.; Honda, Y. *J. Am. Chem. Soc.* **1984**, *106*, 262.

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crystal structure of the macrocyclic tetrathionolactone $(-CH_2CH_2C(S)O-)_4$ shows this molecule to adopt a [4444] conformation in which the ester groups are endocyclic.[21] Molecular mechanics calculations on the related tetralactone $(-CH(CH_3)CH_2C(O)O-)_4$ indicate the same [4444] conformation is the lowest energy form for this molecule.[21] Note that an exodentate [4444] conformation for 16S4 completely disfavors chelation. In order to complex metal ions in an encircling fashion, coordination of one of the sulfur atoms probably occurs first, and then a complete conformational rearrangement evidently must occur in order to bring the other sulfur atoms into contact with the metal center.[22]

The molecular mechanics calculations in this work are in agreement with expectation (see above); the exodentate [4444]A conformation is more stable than either of the endodentate [4444] conformations, [4444]B and [4444]C (see Figure 1). Note that energy differences between the three [4444] conformations are relatively small (<1 kcal/mol). All three of the [88] conformations and the three "crown" type conformations are significantly higher in energy than the [4444] conformations.

The coordination geometry around the metal center in $[Hg(16S4)](ClO_4)_2$ and $[Cd(16S4)](ClO_4)_2$ can be described as elongated octahedra with perchlorate oxygens occupying the apical positions (see below). The conformations adopted by the 16S4 ligand in $[Hg(16S4)](ClO_4)_2$ is [4444]C, an endodentate conformation, while that adopted by the ligand in $[Cd(16S4)](ClO_4)_2$ is best described as [88]C. Note that, in order to complex these metals, the ligand must adopt higher energy conformations, a cost of 0.83 kcal/mol ([4444]A → [4444]C) and 5.52 kcal/mol ([4444]A → [88]C), respectively.[23]

The structure of $[Cd(16S4)](ClO_4)_2$, as revealed by this study, is one involving a nearly square-planar array of sulfur atoms around the metal center provided by the encircling tetradentate macrocyclic ligand. The perchlorate anions occupy apical positions to complete the elongated octahedral geometry. Note that in this structure the Cd(II) complex is located on a crystallographic inversion center.

The X-ray crystal structure of $[Hg(16S4)](ClO_4)_2$ in this study, as in the one reported by Jones and co-workers,[10] shows the Hg(II) ion to be encircled by the macrocyclic tetrathioether ligand with the "Hg coordination sphere completed by apical perchlorate anions". These two crystal structures are different, however. The structure reported by Jones et al.[10] shows a monoclinic $P2_1$ space group with $Z = 2$. The structure from this present study, on the other hand, has the centered monoclinic space group $C2/c$ with $Z = 4$. Thus, the complex in this present structure is located on a crystallographic 2-fold rotation axis. A comparison of the structural features between these two $[Hg(16S4)](ClO_4)_2$ structures, as well as other complexes of 16S4, is summarized in Table VI.

Thermal parameters for the ligand atoms in $[Hg(16S4)](ClO_4)_2$ show a large degree of motion for this molecule, due, perhaps, to a slight rotational disorder about the mercury atom. The ligand appears to be wiggling about the axis perpendicular to the plane of the macrocycle. This thermal motion may reflect a flat or very broad minimum of the motion of the macrocycle and may be responsible for the relatively high R value observed for this structure.[24] Since the thermal ellipsoids of the ligand are "concentric" with the macrocycle and not perpendicular to the plane of the macrocycle, the disorder would appear *not* to be a "conformational disorder" of the ligand. In addition, the ellipsoids do not have long axes in the same general direction, which would seem to rule out crystal dynamics as a contributor to the disorder.

Note that although the structures of both $[Hg(16S4)](ClO_4)_2$ and $[Cd(16S4)](ClO_4)_2$ are described as elongated octahedra, the perchlorate oxygens are clearly not coordinated to the metal ion. The Hg–O bond length of 2.75 (1) Å and the Cd–O bond length of 2.434 (4) Å are both longer than the sum of their respective covalent radii (2.22 Å for Hg–O and 2.21 Å for Cd–O[25]). The infrared bands for the perchlorates in these complexes (a strong, broad band at 1140–1170 cm^{-1} and a sharp band at about 620 cm^{-1}) are also indicative of uncoordinated perchlorate anions; they are identical with those observed for $KClO_4$. Conditional stability constants for Cu(II) complexes of several macrocyclic tetrathioethers have indicated increased complex stability with increased perchlorate anion concentration.[26] These results have been interpreted as indicating 1:1 interaction, in solution, between perchlorate and the Cu(II)–tetrathioether complex by way of perchlorate–Cu(II) coordination. It may be that perchlorate coordination is important in Cd(II) and Hg(II) tetrathioether complexes in solution, but there is apparently no "inner-coordination sphere" association in the solid state.

The Hg–S bond lengths in $[Hg(16S4)](ClO_4)_2$ are comparable to those observed in (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane)bis(dichloromercury(II))[27] (Hg–S average = 2.60 Å), $[Hg(14S4)(OH_2)](ClO_4)_2$[28] (Hg–S average = 2.60 Å), or $(14S4){\cdot}2HgCl_2$[28] (Hg–S average = 2.64 Å) and are significantly shorter than the Hg–S bond lengths in the octahedral complex $[Hg(9S3)_2](ClO_4)_2$ (Hg–S average = 2.68 Å).[29] An increase in bond length is generally observed in increasing coordination number so the longer Hg–S bonds in the octahedral 9S3 complex are not unexpected. Thus, the ionic radius for tetrahedral (CN = 4) Hg^{2+} is 1.10 Å, while that for octahedral (CN = 6) Hg^{2+} is 1.16 Å.[30]

The six-membered chelate rings in the Cd(II) structure adopt both chair and twist-boat conformations. Thus, there are two chair cyclohexane rings sharing a common Cd atom and two twist-boat rings, a consequence of the conformation of the macrocycle, [88]C. This same conformation is seen in the structure of $[Cu(16S4)](ClO_4)_2$.[31] The Hg(II) structure, on the other hand, has all of the six-membered chelate rings adopting twist-boat conformations and no chair forms, as was also found in the earlier structure.[10] It may be that the presence of higher energy boat forms for the chelate rings, coupled with the inherent preference for an exodentate conformation of the macrocyclic polythioether, contributes to the lack of a macrocyclic effect in this polythioether ligand. Note that while the endodentate [4444]C conformation is lower in energy than the corresponding endodentate [88]C (by 4.69 kcal/mol), a price must be paid in the corresponding metal

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(23) A complete conformation analysis including the bound metal (monodentate, bidentate, etc.) would be very informative. Unfortunately, MM2 does not currently include parameters for either Hg or Cd. Calculations on the free ligand are still useful, however, as steric interactions in the macrocyclic ligand itself such as bond stretching, bending, van der Waals interactions, gauche interactions, etc. are still present. Molecular mechanics calculations on Cu(II) complexes of various macrocyclic polythioethers have been carried out: Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1984**, *23*, 1591. For an excellent discussion on the structural aspects of macrocyclic ligands and their transition-metal complexes (especially nitrogen donor atoms) see: Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; Chapter 4.

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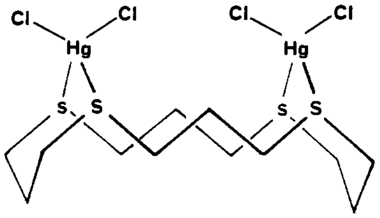
Table VI. Comparison of Structural Features of Complexes of 16S4

complex	av M–S, Å	av S–M–S,[g] deg	ligand conformn	chelate ring conformn
$[Hg(16S4)](ClO_4)_2$[a]	2.616	91.5 161.6	[4444]C	twist-boat
$[Hg(16S4)](ClO_4)_2$[b]	2.597	91.7 161.6	[4444]C	twist-boat
$[Cd(16S4)](ClO_4)_2$[b]	2.618	90 180	[88]C	chair twist-boat
$[Cu(16S4)](ClO_4)_2$[c]	2.359	90 180	[88]C	chair twist-boat
$[Mo_2(SH)_2(16S4)](CF_3SO_3)_2 \cdot 2H_2O$[d]	2.450	89.7 170.5	crown C	chair
$[MoO(SH)(16S4)](CF_3SO_3)$[e]	2.478	89.9 176.5	crown C	chair
$[Mo(N_2)_2(Me_8 16S4)]$[f]	2.424	89.9	crown C	chair

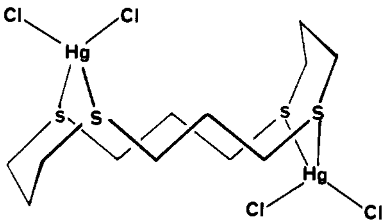
[a] Reference 9a. [b] This work. [c] Reference 31. [d] Reference 32. [e] Reference 33. [f] Reference 34. [g] Note that the coordination geometry in each of these complexes is approximately square planar.

complex in terms of the number of twist-boat chelate rings.[23] Interestingly, the molybdenum complexes of 16S4 $[Mo_2(SH)_2(16S4)](CF_3SO_3)_2 \cdot 2H_2O$[32] and $[MoO(SH)(16S4)](CF_3SO_3)$,[33] as well as $[Mo(N_2)_2(Me_8 16S4)]$,[34] all crystallize with the ligand adopting a crown type conformation, which results in chair conformations for all of the chelate rings. Note that the crown conformations (Figure 1) are relatively high in energy.

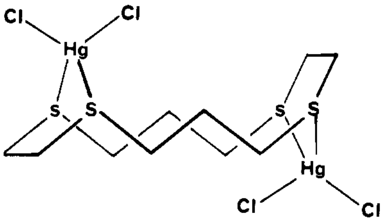
The 16S4 complex of mercuric chloride, $(16S4)(HgCl_2)_2$, most likely involves tetrahedrally coordinated Hg atoms with each Hg bonded to two chlorines and two sulfurs. Structural possibilities include **1** and **2**, in which the $HgCl_2$ moieties are syn and anti, respectively. Note that the X-ray crystal structure of $(14S4)(HgCl_2)_2$ involves two tetrahedrally coordinated Hg atoms in an anti rearrangement with respect to the macrocyclic ring.[28] Since tetrahedrally coordinated $HgCl_2$ units are also found in the crystal structure of dichloro(1,3,5-trithiane)mercury(II), $(6S3)(HgCl_2)$.[35]



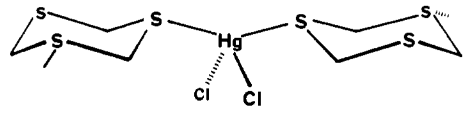
1



2

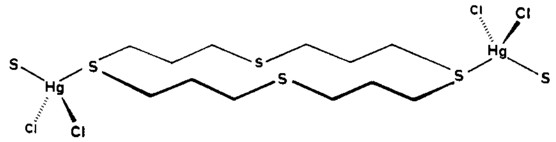


$(14S4)(HgCl_2)_2$



$(6S3)(HgCl_2)$

Note that structural possibilities **1** and **2** involve bidentate coordination of the thioether ligand with each Hg(II). Another possibility may be monodentate coordination of each sulfur atom such that the ligand serves as a bridging monodentate ligand, **3**. Such a structure has been observed in $(14S4)(HgI_2)$[36] as well as $(6S3)(HgCl_2)$.



3

Another structural possibility might involve coordination of one $HgCl_2$ unit to two sulfur atoms of the macrocyclic tetrathioether and coordination of the second $HgCl_2$ with the first $HgCl_2$ unit by way of bridging chlorine atoms and not by coordination to thioether sulfurs. Such mercury coordination has been observed in (1,6-dithiacyclodeca-3,8-diene)bis(dichloromercury(II))[37] and (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane)bis(dichloromercury(II)).[27] Coordination of this type seems unlikely here; coordination of the second $HgCl_2$ moiety with sulfur rather than with $HgCl_2$ is more reasonable. There may well be Hg–Cl–Hg bridging in this complex, however. The compound precipitates immediately from the reaction mixture and is very insoluble in polar organic solvents (nitromethane, acetonitrile), suggesting a network polymeric structure.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, thermal parameters, bond lengths, and bond angles and additional ORTEP and PLUTO views of the structures (13 pages); listings of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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